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CLAIMS

1. Photosensitive adhesive composition of polymerizable resin type whose hardening is obtained by polymerization and/or cross-linking **characterized** in that said composition contains:

- 5 - means for initiating at least one chain polymerization reaction in order to ensure hardening of said composition, and
- a sufficient quantity of at least one bifunctional monomer including firstly a photocleavable centre comprising at least one photocleavable unit, and secondly at least two
- 10 polymerizable units linked by covalent skeletons to said photocleavable centre and positioned either side of the cleavage site or sites of said photocleavable centre so that said hardened composition loses its integrity and adhesiveness under the action of uncrosslinking radiation which causes cleavage of the
- 15 photocleavable units.

2. Adhesive composition as in claim 1 **characterized** in that the initiation means for radical reaction are photoinitiating means consisting of at least one photoinitiator

20 able to initiate the radical reaction mechanism of crosslinking under the action of crosslinking radiation whose wavelength λ_1 is different to wavelength λ_2 for uncrosslinking radiation.

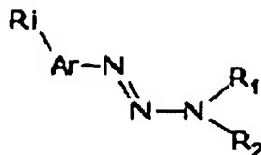
3. Adhesive composition as in either of claims 1 or 2,

25 **characterized** in that the photocleavable unit of the photocleavable centre is of arylazophosphonate type, and in that the bifunctional monomer is chosen from among: 1,5-bis[4'-(methacryloylmethyl)phenylazomethyl-phosphonate]-diethylene glycol; 1,5-bis[4'-(methyl glycidyl ether)phenylazomethyl-phosphonate]-diethylene glycol.

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4. Adhesive composition as in either of claims 1 or 2, **characterized** in that the photocleavable units of the photocleavable centre are aryl-triazene units having the formula:

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in which:

- Ar designates an aromatic system, monocyclic or polycyclic, carbocyclic or heterocyclic, including atoms such as S or N in particular, each cycle preferably comprising 5 or 6 atoms, and is the remainder of an aromatic amine,

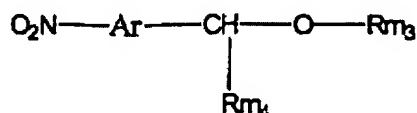
- Ri is chosen from among the following groups: alkyl whether linear or branched, saturated or unsaturated, optionally substituted, aryl whether aromatic or heteroaromatic, substituted or unsubstituted, alkoxy such as methoxy for example or ethoxy, aryloxy, alkylthio, arylthio, benzyl, halogeno, hydroxy, hydroxyalkyl, thiol, alkyloxycarbonyl, aryloxycarbonyl, cyano, carbonyl, formyl, amino, carboxylic and sulfonic ester, carboxylic sulfonic and phosphoric amide, carboxylic sulfonic and phosphoric acid, sulfonate, phosphonate, -CONR'R'' group or -OCO₂R', -OSO₂R', -OPOOR'OR'', -R'NHCOOR'', -R'OCO₂R'', -NR'R'' (in which R' and R'' represent an alkyl group, a carbocyclic or heterocyclic group, aliphatic, unsaturated, a (hetero-)aromatic group, all substituted or unsubstituted, imine whether substituted or not, nitro, -N=N-R', -R_p-Si-(OR_q)₃ group (in which R_p is a hydrocarbon chain, preferably a linear alkyl chain comprising at least 3 C atoms, and R_q denotes a hydrogen atom, a hydroxy group, a C1-C6 alkoxy chain or a -(Si(OR_q) group), a vinyl group, an acrylic group, an alkyloxycarbonyl group, an aryltriazene group,

- R1 and R2 are chosen independently from one another, a -N=N-R' group, -NR'-N=N-R'' group, OH group, NR'R'' group, (R' and R'' have the previously given denotations), an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, an alkoxy group substituted or not, a benzyl group, a (hetero)-aromatic group, all substituted or not by substituents of Ri type, a

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hydroxyethyl, cyanoethyl, aminoethyl, acryloxyethyl, halogenoethyl group.

5 5. Adhesive composition as in either of claims 1 or 2, **characterized** in that the photocleavable unit(s) of the photocleavable centre are 2-nitrobenzyl units having the formula:



10 in which:

- Ar designates an aromatic or heteroaromatic radical (including an atom such as N or S for example) monocyclic or polycyclic and carrying at least one Rk substituent

15 - Rk designates an auxochromic or bathochromic substituent which may be chosen from the following examples: hydrogen, halogen, alkyl chain, aliphatic acyclic saturated or unsaturated, linear or branched, a cyclic, aliphatic, unsaturated, aromatic or heteroaromatic radical preferably having 5 to 14 atoms, preferably 5 to 6, these chains and radicals possibly being substituted, interrupted or terminated by a heteroatom such as B, N, O, Si, P, S or a halogen, a nitro group, cyano group, an alkoxy, aryloxy, alkylthio, arylthio, benzyl, alkyl, hydroxy, thiol, alkyloxycarbonyl, aryloxycarbonyl, carbonyl, formyl, amino radical, carboxylic ester, amide, sulfonic ester, sulfonic amide, 20 carboxylic acid, sulfonic acid, sulfonate, phosphonate, a - OCONR'R'' group, -OCO₂R', -OSO₂R', -OPOOR'OR'', -R'NHCOOR'', R'OCO₂R'', NR'R'' (R' and R'' are an alkyl, aryl group, a carbocyclic or heterocyclic group), imine substituted or unsubstituted, diazo -N=N-R', -Rp-Si(ORq)₃ group (Rp and Rq as 25 defined in claim 4), alkylglycidyl ether, alkylvinyl ether, cyclohexyl epoxy.

- R_{m4} is chosen from among a hydrogen, an alkyl, alkenyl, alkenyl, alkylaryl chain, all substituted or unsubstituted, preferably C1-C6, a carbocyclic or heterocyclic chain saturated

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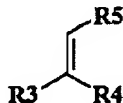
or unsaturated, aromatic or heteroaromatic, substituted or unsubstituted, preferably having 5 to 14 atoms, preferably 5 to 6, an alkoxy, aryloxy, alkylthio, arylthio chain, an alkyloxocarbonyl group, -NR'COR'' group, -OCOR' group, -OCOOR' group, -OCONR'R'' group, NR'COOR'' group, -OPOR'R''R''' group, -OSO₂R' group, -OPOOR'OR'' group, -NR'R'', -COOR'group, -CONR'R'', SOOR', -COR' group (R' and R'' have the previously indicated denotations), an imine group substituted or unsubstituted, a hydroxy, thiol group, a carboxylic acid or derivative of carboxylic acid, a halogen, a nitrile, an alkyl(C1-C6)glycidyl ether group, alkyl(C1-C6)vinyl ether group, cyclohexyl epoxy, -Rp-Si-(ORq)₃ group (Rp and Rq as in claim 4).

- R_{m3} is chosen from among a hydrogen, an alkyl, alkenyl, alcyanyl, alkylaryl chain, all substituted or unsubstituted, interrupted by a heteroatom such as N, O, P, Si, S, preferably C1-C6, a carbocyclic or heterocyclic chain, saturated or unsaturated, aromatic or heteroaromatic, substituted or unsubstituted, preferably having 5 to 14 atoms, preferably 5 to 6, an alkyloxocarbonyl group, NCOOR' group, -POR'R''R''' group, -SO₂R' group, -POOR'OR'' group, -COOR' group, -CONR'R'', COR' group (R', R'' and R''' having the previously indicated denotations for R' and R'' in claim 5), an alkyl(C1-C6)glycidyl ether group, alkyl(C1-C6)vinyl ether group, cyclohexyl epoxy, -Rp-Si(ORq)₃ group (Rp and Rq as defined in claim 4).

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6. Composition as in any of claims 1, 2, 4 to 5 **characterized** in that the polymerizable units of the bifunctional monomer are radically polymerizable and are vinyl groups defined by formula IV:

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in which R3, R4, R5 are substituents able to activate together the double vinyl bond vis-à-vis radical addition chain

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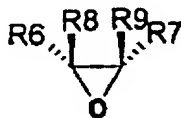
reactions, at least one of said substituents being a hydrocarbon chain advantageously a C1-C6 alkyl chain.

7. Composition as in the preceding claim, **characterized** in that at least one of the substituents R3, R4 and R5 is chosen from among the groups: aryl, carbonyloxyalkyl, carbonyloxyaryl, carboxy (-COOH), alkoxy-carbonyl (-O₂CR), carbamoyl (-CONR₂) and cyano.

8. Composition as in any of claims 2 to 6 **characterized** in that the bifunctional monomer comprises at least two types of complementary vinyl units, capable of creating a charge transfer complex (electron donor/acceptor pair) itself able to initiate a radical reaction under the action of crosslinking radiation of wavelength λ_1 , or at least one type of acceptor vinyl unit able to create a charge transfer with another complementary species.

9. Composition as in the preceding claim, **characterized** in that the donor vinyl unit is chosen from among the elements: styrene, vinyl acetate, vinyl ether, exomethylene dioxolane in particular 4-methylene-2-phenyl-1,3-dioxolane, alkyl methacrylate, vinyl pyrrolidone, vinyl carbazole, vinyl naphthalene, while the vinyl unit of acceptor type is chosen from among: maleic anhydride, acrylonitrile, diethyl fumarate, fumaronitrile, maleimides.

10. Composition as in any of claims 1, 2, 4 to 5 **characterized** in that the polymerizable units of the bifunctional monomer are cationically polymerizable and are oxirane groups defined by formula V:

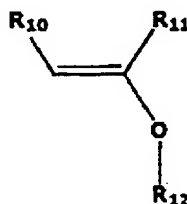


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in which at least one of the substituents R6, R7, R8, R9 is a hydrocarbon chain and are chosen from among a hydrogen atom, halogen atom, an alkyl, alkoxy, alkylthio chain linear or branched, saturated or unsaturated, acyclic or cyclic, preferably
 5 C1-C6, optionally substituted, optionally interrupted by a heteroatom, an aromatic or heteroaromatic aryl group, an aryloxy or arylthio group preferably having 5 to 6 atoms, a benzyl group, imine group, amino NR'R'', SiR'R''R''', alkyl(C1-C6)oxycarbonyl, aryl(C1-C6)oxycarbonyl, amide, carboxylic and sulfonic ester,
 10 sulfonate, phosphonate, a carbonyl group, cyano, -CONR'R'' group, -OCO₂R' group, -OSO₂R' group, -OPOOR'OR'' group, -R'NHCOOR'', R'OCO₂R'' in which R', R'', R''' represent an alkyl group (preferably C1-C6) substituted or unsubstituted, aryl (preferably having 5 to 6 atoms), carbocyclic or heterocyclic
 15 group, aliphatic, unsaturated or aromatic, substituted or unsubstituted.

11. Composition as in the preceding claim, **characterized** in that, for reasons of steric hindrance, two of the substituents
 20 R6, R7, R8, R9 are a hydrogen atom.

12. Composition as in any of claims 1, 2, 4 to 5 **characterized** in that the polymerizable units of the bifunctional monomer are cationically polymerizable and are vinyl ethers
 25 defined by formula VI:



in which:

30 - R10 and R11 are the same or different and designate a hydrogen atom or advantageously a linear or branched C1-C6 alkyl

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chain, substituted or not, saturated or unsaturated, acyclic or cyclic, optionally interrupted by a heteroatom such as O, N, Si, P for example, an aromatic or heteroaromatic aryl group (preferably having 5 to 6 atoms), an alcoxy chain (preferably C1-C6), alkylthio chain (preferably C1-C6), arylthio (preferably having 5 to 6 atoms).

- R12 advantageously designates a linear or branched C1-C6 alkyl chain, substituted or not, saturated or unsaturated, acyclic or cyclic, optionally interrupted by a heteroatom such as O, N, S, Si, P for example, an aromatic or heteroaromatic aryl group (preferably having 5 to 6 atoms).

13. Composition as in any of claims 1 to 12, **characterized** in that the bifunctional monomer is of oligomer or prepolymer size and has a comb branch structure, consisting of a principal linear polymer chain of which each of the comb branches contains at least one photocleavable unit positioned on the side of the principal chain and at least one polymerizable unit positioned at the free end of the branch.

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14. Composition as in the preceding claim, **characterized** in that the comb branches contain a photocleavable unit and a polymerizable unit.

25 15. Composition as in any of claims 1 to 12, **characterized** in that the bifunctional monomer is of oligomer or prepolymer size and has a hyperbranched structure.

16. Composition as in the preceding claim **characterized** in that the bifunctional monomer with hyperbranched structure is synthesized from a precursor monomer of AB₂ or AB₃ type, in particular under a polycondensation mechanism.

17. Adhesive composition as in either of claims 15 or 16, **characterized** in that the hyperbranched structure has a core

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comprising photocleavable units, and a peripheral shell consisting of inert units from a photochemical viewpoint.

18. Adhesive composition as in either of claims 15 or 16, **characterized** in that the hyperbranched structure has a core consisting of inert units from a photochemical viewpoint, and a peripheral shell comprising photocleavable units.

19. Adhesive composition as in claims 1, 4 and 6, **characterized** in that the bifunctional monomer is chosen from:
 1,2-Bis[1-(4'-methacryloylmethyl-)phenyl-3-methyl] triaz(1)ene-ethane;
 1,2-Bis[1-(4'-(methacryloylethyl)aminocarbonyloxymethyl)phenyl-3-methyl-]triaz(1)ene-ethane;
 1-(4'-methacryloylmethyl-) phenyl-3-(2'-methacryloylethyl)-3-methyl-triaz(1)ene;
 1-(4'-(methacryloylethyl)aminocarbonyloxymethyl)phenyl-3-((methacryloylethyl) aminocarbonyloxyethyl) -3-methyl-triaz(1)ene;
 1-(4'-methacryloylmethyl-)phenyl-3,3-di(2'-methacryloylethyl) -triaz(1)ene;
 1-(4'-(methacryloylethyl)aminocarbonyloxymethyl)phenyl-3,3-di((methacryloylethyl)aminocarbonyloxyethyl)-triaz(1)ene;
 1-(3'-methacryloylethyl carboxyphenyl)-3-di(2'-methacryloylethyl)triaz(1)ene;
 1,2-Bis[1-(3'-methacryloylethylcarboxyphenyl)-3-methyl]triaz(1)ene-ethane;
 2-methacryloylmethyl-5-(3'-(2'-methacryloylethyl)-3'-methyl)triaz(1)ene-thiophene.

20. Adhesive composition as in claims 1, 4 and 10, **characterized** in that the bifunctional monomer is chosen from among:
 1-(3'-ethyl glycidyl ether carboxyphenyl)-3-(ethyl glycidyl ether)-3-methyl-triaz(1)ene,
 1-(3'-ethyl glycidyl ether carboxy-6'-methylphenyl)-3-(ethyl glycidyl ether)-3-methyl-triaz(1)ene;
 1-(4'-methyl glycidyl ether)-3-(ethyl glycidyl ether)-3-methyl-triaz(1)ene.

21. Adhesive composition as in claims 1, 5 and 6, **characterized** in that the bifunctional monomer is chosen from

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among: 2-Methyl-acrylic acid 5-methoxy-4-[2-(2-methyl-acryloyloxy)-ethoxy]-2-nitro-benzyl ester; 2-Methyl-acrylic acid 1-(5-methoxy-4-[2-methyl-acryloyloxy)-ethoxy]-2-nitro-phenyl)-ethyl ester; 2-Methyl-acrylic acid 4,5-bis-[2-(2-methyl-acryloyloxy)-ethoxy]-2-nitro-benzyl ester; 2-Methyl-acrylic acid 2-(5-methoxy-4-(2[2-(2-methyl-acryloyloxy)-ethoxycarbonyloxy]-ethoxy)-2-nitro-benzloxycarbonyloxy)-ethyl ester.

22. Adhesive composition as in claims 1, 5 and 10, **characterized** in that the bifunctional monomer is chosen from among: 2-[2'-nitro-4',5'-di(oxy-methyloxirane)]benzyloxymethyl oxirane; (2-Methoxy-5-nitro-4-oxiranylmethoxymethyl-phenoxy)-acetic acid oxiranylmethyl ester.

23. Adhesive composition as in claims 1 and 13 or 14 **characterized** in that the bifunctional monomer is chosen from:

- Poly[(14-(2'-aminoacylethyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co(7-(2'-4'-aminoacylethyl)-1,4-dioxa-5-oxo-6-aza-heptane)],
- 20 • Poly[(14-(4'-aminoacylhexyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(4'-aminoacylhexyl)-1,4-dioxa-5-oxo-6-aza-heptane)],
- Poly[(14-(4'-(4''-aminoacylphenyl)methylphenyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-
25 (7-(4'-(4''-aminoacylphenyl)methylphenyl)-1,4-dioxa-5-oxo-6-aza-heptane)],
- Poly[(14-(4'-(4''-aminoacylcyclohexyl)methylcyclohexyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-
30 (7-(4'-(4''-aminoacylcyclohexyl)methylcyclohexyl)-1,4-dioxa-5-oxo-6-aza-heptane)],
- Poly[(14-(4'-methylaminoacylcyclohexyl)-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(4'-methylaminoacylcyclohexyl)-1,4-dioxa-5-oxo-aza-heptane)],

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- Poly[(14-(4'-aminoacylbutyl-6-(hydroxymethyl)-1,4,8,11-tetraoxa-12-oxo-13-aza-tetradecane)-co-(7-(4'-aminoacylbutyl)-1,4-dioxa-5-oxo-6-aza-heptane)]
- in which all these polymers are esterified on the hydroxy group at position 6 of the copolymer chain by groups of type:
 - -oxycarbonyl-3-[3'-(2''-(methacrylate)ethyl))-3'-methyl-triazene]phenyl
 - oxycarbonyl-ethyloxy-(1-methoxy-3-(methacrylatemethyl)-4-nitro)phenyl.

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24. Adhesive composition as in claims 1 and 17, **characterized** in that the bifunctional monomer is chosen from among:

- Poly(1-(3'-carboxyphenyl)-3-,3-di(2''hydroxyethyl)triazene),
- Poly(1-(3'-carboxy-6'-methylphenyl)-3-,3-di(2''-hydroxyethyl)triazene)
- Poly(1-(4'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene),
- 20 • Poly(1-(3',5'-dicarboxyphenyl)-3-(2''-hydroxyethyl)-3-methyl -triazene),
- Poly(1-(3'-carboxyphenyl)-3-,3-di(2''-hydroxyethyl)triazene-co-2,2-bis(hydroxymethyl)propionic acid),
- Poly(1-(3'-carboxy-6'-methylphenyl)-3-,3-di(2''-hydroxyethyl)triazene-co-2,2-bis(hydroxymethyl)propionic acid),
- 25 • Poly(1-(4'carboxyphenyl)-3-,3-di(2''hydroxyethyl)triazene-co-2,2-bis(hydroxymethyl)propionic acid),

ω-functionalized by methacrylate ends with methacrylic acid and its derivatives, such as 2-hydroxyethylmethacrylate, glycidyl methacrylate or 2-isocyanatoethyl methacrylate for example, or oxirane ends of glycidyl type by reaction with an epihalohydrine for example.

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25. Adhesive composition as in claims 1 and 18 **characterized** in that the bifunctional monomer is chosen from among:

- Poly(2,2-bis(hydroxymethyl)propionic acid -co-1-(3'-carboxy phenyl)-3-,3-di(2''-hydroxyethyl)triazene),
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- Poly(2,2-bis(hydroxymethyl)propionic acid -co-(3'-carboxy-6'-methyphenyl)-3-,3-di(2''-hydroxyethyl)triazene),
- ω -functionalized by methacrylate ends with methacrylic acid and its derivatives, such as 2-hydroxyethylmethacrylate, glycidyl methacrylate or 2-isocyanatoethyl methacrylate for example, or by
10 oxirane ends of glycidyl type by reaction with an epihalohydrine for example.
- Poly(2,2-bis(hydroxymethyl)propionic acid),
 ω -functionalized by an oxycarbonyl-3-[3'-(2''-(meth
15 acrylate)ethyl))triazene]phenyl group or an -oxycarbonyl-ethyl oxy-(1-methoxy-3-(methacrylatemethyl)-4-nitro)phenyl group.

26. Adhesive composition as in any of claims 2 to 25, **characterized** in that the photoinitiation means also comprise a
20 co-initiator.

27. Adhesive composition as in any of claims 2 to 26, **characterized** in that the photoinitiation means comprise at least one species able to cause their photo-sensitization.

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28. Adhesive composition as in any of claims 1, 3 to 25, **characterized** in that the initiation means of the chain polymerization reaction(s) are of chemical type.

30 29. Bifunctional monomer including firstly a photocleavable centre comprising at least one photocleavable unit, and secondly at least two polymerizable units linked by covalent skeletons to said photocleavable centre and positioned either side of the cleavage site or sites of said photocleavable
35 centre, characterized in that it is of oligomer or prepolymer size and has a comb branched structure consisting of a principal

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linear polymer chain of which each of the comb branches contain at least one photocleavable unit positioned on the side of the principal chain and at least one polymerizable unit positioned on the free end of the branch.

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30. Bifunctional monomer including firstly a photocleavable centre comprising at least one photocleavable unit, and secondly at least two polymerizable units linked by covalent skeletons to said photocleavable centre and positioned
10 either side of the cleavage site or sites of said photocleavable centre, characterized in that it is of oligomer or prepolymer size and has a hyperbranched structure obtained by polycondensation of precursor monomers of AB₂ or AB₃ type.

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31. Bifunctional monomer as in claim 30, **characterized** in that the hyperbranched structure has a core comprising photocleavable units, and a peripheral shell consisting of inert units from a photochemical viewpoint.

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32. Bifunctional monomer as in claim 30, **characterized** in that the hyperbranched structure has a core consisting of inert units from a photochemical viewpoint, and a peripheral shell comprising photocleavable units.

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33. Method for preparing a bifunctional monomer including firstly a photocleavable centre comprising at least one photocleavable unit, and secondly at least two polymerizable units linked by covalent skeletons to said photocleavable centre and positioned either side of the cleavage site or sites of said
30 photocleavable centre, **characterized** in that it comprises in this order:

- a synthesis step of the photocleavable centre,
- a structural arrangement step of the photocleavable centre,
- 35 - an association step associating polymerizable units with the photocleavable centre.

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34. Method as in claim 33, **characterized** in that it comprises a synthesis step of a photocleavable aryl-triazene unit consisting of:

- 5 - conducting diazotation in inert organic medium in the presence of a Lewis acid of type BF_3 or PF_5 or SbF_5 and of an organic nitrite,
- then conducting diazoic coupling by adding a compound comprising at least one primary or secondary amino group, in a
10 dissociating organic medium in the presence of a mineral compound of sodium carbonate, potassium carbonate or sodium hydrogenocarbonate type.

35. Method as in claim 33, **characterized** in that it
15 comprises a creation step to create polymerizable units of vinyl type on the photocleavable centre, consisting of the creation of acryloyl functions by nucleophilic substitution on acryloyl carbon, in particular via a mechanism of nucleophilic or basic catalysis.

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36. Method as in claim 33, **characterized** in that it comprises a grafting step to graft vinyl type polymerizable units onto the photocleavable centre, consisting of grafting the vinyl function included in a molecule comprising at least one reactive
25 function (F1) to the chemical skeleton of the photocleavable centre, and also comprising at least one other reactive function (F2), by causing these two functions to react via a nucleophilic substitution mechanism on an acyl group carbon under conditions of nucleophilic or basic catalysis.

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37. Method as in the preceding claim, **characterized** in that one of the two reactive functions (F1,F2) is an OR group or an -OOCR group.

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38. Use of the photosensitive adhesive composition as in claims 1 to 28 for various clinical applications in the area of

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dentistry, in particular to bond elements to the surface of teeth and/or to seal tooth cavities.